



# Thermal degradation of Fenitrothion: Identification and eco-toxicity of decomposition products

Roberto Sanchirico<sup>a,\*</sup>, Gabriele Pinto<sup>b</sup>, Antonino Pollio<sup>b</sup>, Mauro Cordella<sup>c</sup>, Valerio Cozzani<sup>c</sup>

<sup>a</sup> Istituto di Ricerche sulla Combustione (CNR), P.le Tecchio, 80, 80125 Napoli, Italy

<sup>b</sup> Dipartimento di Scienze Biologiche, sezione di Biologia Vegetale, Università di Napoli "Federico II", Via Foria 223, 80139 Napoli, Italy

<sup>c</sup> Dipartimento di Ingegneria Chimica, Mineraria e delle Tecnologie Ambientali, Alma Mater Studiorum – Università di Bologna, via Terracini, 28, 40131 Bologna, Italy

## ARTICLE INFO

### Article history:

Received 27 April 2011

Received in revised form

30 September 2011

Accepted 8 November 2011

Available online 17 November 2011

### Keywords:

Fenitrothion

Thermal decomposition

Calorimetry

Eco-toxicity

ECOSAR

## ABSTRACT

The thermal decomposition of Fenitrothion [phosphorothioic acid O,O-diethyl O-(3-methyl-4-nitrophenyl) ester] was investigated. Results obtained by different scale calorimetric techniques show that the thermal decomposition of Fenitrothion involves two main steps. Intermediate and final thermal degradation products formed during isothermal and adiabatic thermal decomposition experiments were identified. The eco-toxicological profile of the decomposition products was assessed experimentally and compared to results obtained with a predictive software (ECOSAR). A specific index was defined to assess the change in ecotoxicity profile of decomposition products with respect to the original compound.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

The hazard related to the storage and handling of pesticides is well known [1,2]. Toxicity, thermal instability and reactivity caused several accidents during the production, the transport and the storage of these compounds [3]. Particularly severe accidents were caused by the atmospheric dispersion of decomposition products formed as a consequence of fire or of runaway during storage or mixing processes [4,5]. The Seveso accident [6], that gave the name to the European Directive on the control of major accident hazards involving dangerous substances [7], is a well known example of the very severe hazards that may derive from these accidental scenarios. Several studies proposed methods for the identification of possible unwanted products formed in "out of control" conditions, mainly starting from past accident analysis, from the definition of experimental protocols and from simple predictive methodologies [4,8–12]. However, in spite of the relevant work carried out to develop and standardize experimental protocols and predictive methods, scarce data are often available on the decomposition products that may be formed due to the thermal degradation or partial combustion of chemicals.

In the present study, the thermal degradation and the decomposition products of Fenitrothion were investigated. Fenitrothion

is an organophosphorus compound used to produce pesticides that find a number of applications in agriculture. Production of Fenitrothion is estimated around 15,000–20,000 tonnes/year [13]. Phosphorganic pesticides are well known for their hazard and several accidents related to the formation and dispersion of toxic decomposition products were recorded [14]. Different calorimetric techniques were applied to gather experimental data on the thermal decomposition behaviour of Fenitrothion. The decomposition products were identified by analytical techniques. The possible decomposition pathways of Fenitrothion were examined also on the basis of previous results obtained for dimethoate [15] and ethyl parathion [16]. The eco-toxicity of decomposition products was assessed using both theoretical calculations and experimental bioassays. The results allowed a screening of the hazard related to the possible formation and release of decomposition products in the loss of control of chemical industrial processes involving Fenitrothion. Specific attention was devoted to the comparison of the overall eco-toxicity of the mixture of decomposition products formed, in order to assess the presence and the importance of antagonistic or synergistic effects.

## 2. Experimental

### 2.1. Materials

Fenitrothion (CAS 122-14-5, 97% (w/w) technical purity grade) was purchased by Sigma–Aldrich. Standard samples of the

\* Corresponding author. Tel.: +39 81 7682225; fax: +39 81 5936936.

E-mail address: [r.sanchirico@irc.cnr.it](mailto:r.sanchirico@irc.cnr.it) (R. Sanchirico).

**Table 1**

Compounds identified during the first exothermal event in the isoperibolic (Radex) experiments performed on Fenitrothion.

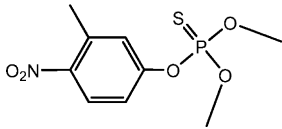
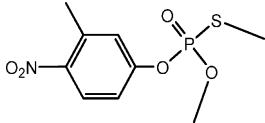
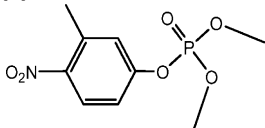
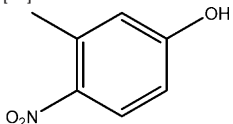
Compound	Name/chemical formula (CF)/molecular weight (MW)/smile
	Fenitrothion O,O-dimethyl O-3-methyl-4-nitrophenyl phosphorothioate (CF: C <sub>9</sub> H <sub>12</sub> NO <sub>3</sub> PS; MW = 277.23) <chem>S=P(OC)(OC)OC1=CC(C)=C([N+](O-)=O)C=C1</chem>
[I] 	O,S-Dimethyl O-3-methyl-4-nitrophenyl phosphorothioate (CF: C <sub>9</sub> H <sub>12</sub> NO <sub>3</sub> PS; MW = 277.23) <chem>O=P(SC)(OC)OC1=CC(C)=C([N+](O-)=O)C=C1</chem>
[II] 	Dimethyl 3-methyl-4-nitrophenyl phosphate (CF: C <sub>9</sub> H <sub>12</sub> NO <sub>6</sub> P; MW = 261.17) <chem>O=P(OC)(OC)OC1=CC(C)=C([N+](O-)=O)C=C1</chem>
[III] 	3-Methyl-4-nitrophenol (CF: C <sub>7</sub> H <sub>7</sub> NO <sub>3</sub> ; MW = 153.14) <chem>OC1=CC(C)=C([N+](O-)=O)C=C1</chem>
[IV]	

Table 1 (Continued)

Compound	Name/chemical formula (CF)/molecular weight (MW)/smile
"Oligomer" (Hypothesis a, b, c, d) [V]	<p><b>Hypothesis a:</b> (CF: C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>O<sub>9</sub>P<sub>2</sub>S<sub>2</sub>; MW = 508.4)  <chem>S=P(OC)(OC1=CC(C)=C([N+](O-)=O)C=C1)SP(OC)(OC2=CC(C)=C([N+](O-)=O)C=C2)=O</chem></p> <p><b>Hypothesis b:</b> (CF: C<sub>23</sub>H<sub>24</sub>N<sub>3</sub>O<sub>12</sub>P<sub>3</sub>S<sub>4</sub>; MW = 755.6)  <chem>S=P(SP(OP(OC)(OC1=CC(C)=C(C=C1)[N+](O-)=O)=S)(OC2=CC(C)=C(C=C2)[N+](O-)=O)=S)(OC3=CC(C)=C(C=C3)[N+](O-)=O)OC</chem></p> <p><b>Hypothesis c:</b> (CF: C<sub>23</sub>H<sub>24</sub>N<sub>3</sub>O<sub>14</sub>P<sub>3</sub>S<sub>2</sub>; MW = 723.5)  <chem>O=P(SP(OC1=CC(C)=C(C=C1)[N+](O-)=O)(OP(OC)(OC2=CC(C)=C(C=C2)[N+](O-)=O)=S)(OC3=CC(C)=C(C=C3)[N+](O-)=O)OC</chem></p> <p><b>Hypothesis d:</b> (CF: C<sub>10</sub>H<sub>15</sub>NO<sub>8</sub>P<sub>2</sub>S; MW = 371.2)  <chem>COP(OP(OC)(OC1=CC(C)=C([N+](O-)=O)C=C1)=O)(OC)=S</chem></p>
a	
b	
c	
d	

decomposition products identified for Fenitrothion, listed in Table 1, were also obtained. Dimethyl 3-methyl-4-nitrophenylphosphate (CAS 2255-17-6) and 3-methyl-4-nitrophenol (CAS 2581-34-2) were purchased by Sigma–Aldrich. Compounds [II] and [V], were not available commercially. A sample representative of compound [V] was obtained by thin layer chromatography (TLC) of samples collected at the end of the first adiabatic decomposition phase. A sample of compound [II] was obtained by TLC starting from a sample collected at the end of an isoperibolic (Radex) run carried out at 413 K for 90 min. The different samples were prepared using as solvent either analytical grade dimethyl sulfoxide (DMSO), for the ecotoxicological bioassay, or methanol, for GC/MS or HPLC analyses. Solvents used in experimental runs were selected on the basis of explorative experiments, in order to maximize the quantitative collection of the residues [16].

## 2.2. Calorimetric techniques

### 2.2.1. Adiabatic calorimetry

Adiabatic runs were carried out using an accelerating rate calorimeter (ARC) by Columbia Scientific Industries. Hastelloy C bombs were used (specific heat  $C_{p,b} = 0.419 \text{ J K}^{-1} \text{ g}^{-1}$ ). The following operating conditions were used for the adiabatic screening of the sample: wait time 10 min; heat step temperature 5 K; initial temperature 323 K; heat rate threshold value  $0.02 \text{ K min}^{-1}$ .

A set of experimental runs was also performed to assess the toxicological profile of the intermediate decomposition products. In these runs the sample was heated to a given initial temperature ( $T_{O,Ad}$ ), the instrument was forced to the adiabatic mode and, after a given time interval the sample was quenched to the final temperature ( $T_{Quenching}$ ). At this temperature the ARC was rapidly open and the bomb cooled at room temperature. The residual sample was then collected using  $25 \text{ cm}^3$  of DMSO and was used for toxicological bioassays.

### 2.2.2. Isoperibolic calorimetry

Isoperibolic experiments were performed using a PC Combilab system (by Systag, CH) devoted to control a Radex Oven [17]. The oven was equipped with a stainless steel reactor having a volume of about  $11 \text{ cm}^3$  and a design pressure of 100 bar at 673 K. Samples of about 2 g were heated at the desired temperature (408, 413 and 423 K) and hold in this condition for the entire run duration. At the end of the run the reactor was quenched at room temperature. Samples for analytical characterization were collected using  $50 \text{ cm}^3$  of methanol.

### 2.2.3. Differential scanning calorimetry (DSC)

A Perkin Elmer 8000 DSC coupled to an Intracooler II cooling system was used to carry out constant heating rate and isothermal runs. Samples of 3–6 mg were charged in a sealed stainless steel high pressure capsule (Perkin Elmer, part number: B0182901) and a purge flow of pure nitrogen ( $20 \text{ cm}^3 \text{ min}^{-1}$ ) was used. Preliminary calibrations were carried out using indium (fusion temperature:  $429.8 \text{ K}$ , fusion heat:  $28.6 \text{ J g}^{-1}$ ) as standard. Dynamic runs were performed starting from 323 K and using heating rates ( $\beta$ ) of 5 or  $10 \text{ K min}^{-1}$  up to 593 K. Isothermal runs were performed at temperatures of 408, 413, 418 and 423 K over different periods of time (190–700 min).

## 2.3. Analytical characterization of decomposition products

Residues collected during the isoperibolic runs were dissolved in methanol and submitted to gas-chromatographic/mass spectrometric (GC/MS) analysis by means of a Varian Saturn 2000 device equipped with an ion trap detector and a DB5 column (length 30 m, internal diameter 0.25 mm, film thickness 0.25  $\mu\text{m}$ ). The flow rate

of the carrier gas (helium) was of  $1 \text{ cm}^3 \text{ min}^{-1}$ . The following temperature ramp was used: 313 K for 1 min,  $10 \text{ K min}^{-1}$  up to 573 K, 573 K for 10 min. The injector temperature was set at 423 K. Raw GC/MS chromatograms and fragmentation patterns of identified peaks are reported in the Supporting Information.

The quantitative characterization runs were carried out using a 1090 Hewlett Packard HPLC equipped with an F5C6 Phenomenex reverse phase column and a diode array detector. The mobile phase was  $\text{CH}_3\text{CN}/\text{aqueous acid buffered solution}$  (67:33) with a flow of  $0.5 \text{ cm}^3 \text{ min}^{-1}$ . The oven temperature was set at 313 K and the signal acquired at 254 and 310 nm. Raw HPLC data and spectra of identified peaks are reported in the Supporting Information.

Gas analysis was performed using a Perkin Elmer Autosystem XL equipped with a packed Carboxen 1000 column (length 5 m, internal diameter 2.1 mm) and a TCD detector. The following temperature ramp was used: 403 K for 3.2 min,  $25 \text{ K min}^{-1}$  up to 513 K. The carrier gas was helium with a flow of  $10 \text{ cm}^3 \text{ min}^{-1}$ .

For the identification of intermediates and of decomposition products, the mixture obtained at the end of the experimental runs was separated by means of silica gel thin-layer chromatography. A toluene/methanol/acetic acid solution (80:15:5) or a mixture of n-hexane/ethyl acetate (70:30) and n-hexane/ethyl ether (50:50) was used as eluents on the basis of previous experiences with similar compounds [16].

## 2.4. Ecotoxicological bioassays

Preliminary dose–response experiments of Fenitrothion (FNT) toxicity towards *Pseudokirchneriella subcapitata* were carried out using either EPA medium [18] or BBM [19]. The results obtained, not reported for the sake of brevity, indicated that salt concentration in the medium does not influence the toxicity of the selected compounds and that in 96-h end-point experiments a higher growth rate of algal biomass was registered with BBM. For this reason all the following experiments were performed with the latter medium.

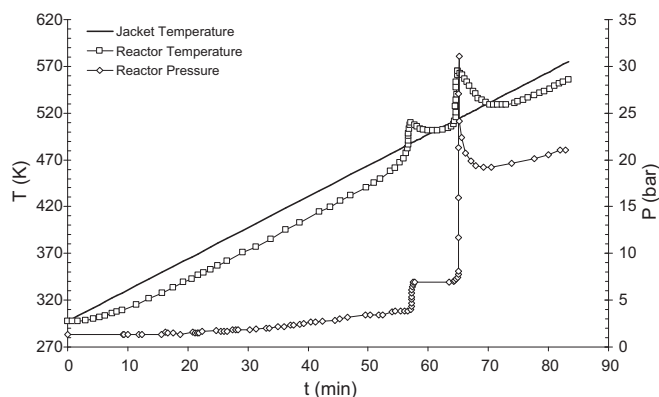
Based on the preliminary results of dose–response experiments, the solutions for the algal bioassays were prepared by dissolving a known quantity of compound in BBM up to a final concentration of  $32 \text{ mg (dm}^3)^{-1}$ . The toxicity tests were based on the measurement of the growth inhibition of the green unicellular alga *P. subcapitata*, strain UTEX 1648 according to EPA guidelines [20]. Algal inocula corresponding to  $10,000 \text{ cells/cm}^3$  from laboratory cultures in mid exponential phase were grown in  $100 \text{ cm}^3$  Erlenmeyer flasks containing a solution composed of  $50 \text{ cm}^3$  of bold basal medium (BBM) and the tested compound at the following concentrations: 32, 16, 8, 4 and  $2 \text{ mg (dm}^3)^{-1}$ . The tested compound was the residual FNT substrate obtained after adiabatic treatment at 409, 416 and 474 K and after isothermal treatment at 413 K at time 0, 75, 120, 150, 195 and 240 min. The flasks were incubated on a shaking apparatus ( $\sim 100 \text{ rpm}$ ) at 297 K and continuously illuminated at a light intensity of  $90 \mu\text{E s}^{-1} \text{ m}^{-2}$ . The tests were carried out in triplicate and in axenic conditions, and a series of control samples containing only BBM and the algal inoculum were also prepared. Negative controls carried out with volumes of DMSO equivalent to those used in the bioassays exhibited no observable effect on *P. subcapitata* growth. The algal growth was assessed after 96 h from the addition of the compounds measuring the in vivo chlorophyll fluorescence using a fluorometer (Turner, model Aquaflor, Turner Designs CA, USA).

Data from growth inhibition tests were analyzed using the software Toxstat 3.4 (Western Ecosystems Technology, Inc., Cheyenne, WY, USA) after verifying normality ( $\chi^2$  test) and homogeneity of variance (Bartlett's test). The  $\text{EC}_{50}$  (96 h) was determined using the ICPIN program [21] which calculates the EC values by linear interpolation and 95% confidence intervals by the bootstrap method.

**Table 2**

Experimental conditions and main results obtained with the dynamic Radex run (see Fig. 1) and the DSC runs (see Fig. 2) carried out on Fenitrothion. DSC results are the average of at least three runs.

Parameter	Radex	DSC	DSC	DSC
Sample initial weight [g]	1.040	$3.3 \times 10^{-3}$	$3.5 \times 10^{-3}$	$3.7 \times 10^{-3}$
Heating rate, $\beta$ [K min <sup>-1</sup> ]	3.33	2.5	10	20
Initial temperature, $T_{\text{Start}}$ [K]	298	323	323	323
Peak temperature of first decomposition step, $T_{R,\text{Peak},1}$ [K]	510	474	501	517
Pressure after first decomposition step, $P_{\text{max},1}$ [bar]	6.9	n.a.	n.a.	n.a.
Heat generated in first decomposition step, $(-\Delta H_{R,1})$ [J g <sup>-1</sup> ]	n.a.	316	359	324
Peak temperature of second decomposition step, $T_{R,\text{Peak},2}$ [K]	565	533	559	574
Pressure after second decomposition step, $P_{\text{max},2}$ [bar]	31.1	n.a.	n.a.	n.a.
Heat generated in second decomposition step, $(-\Delta H_{R,2})$ [J g <sup>-1</sup> ]	n.a.	1770	1987	1993



**Fig. 1.** Thermogram and pressure profile obtained in a Radex scanning run performed on Fenitrothion.

### 3. Results and discussion

#### 3.1. Thermal degradation of Fenitrothion

The thermogram reported in Fig. 1, which is referred to a Radex run performed in scanning mode clearly shows that the decomposition of Fenitrothion develops through two exothermic phases. The experimental conditions and the most significant results obtained during the Radex run are reported in Table 2. A similar behaviour was recorded also in dynamic DSC runs, reported in Fig. 2. Fig. 2(a) reports the baseline-subtracted raw data obtained in a 10 K min<sup>-1</sup> constant heating rate run carried out on a 3.5 mg Fenitrothion sample. The raw DSC curves obtained were then processed subtracting the fictitious baseline obtained by the tangential area-proportional method, shown in Fig. 2(a), in order to evidence only the thermal effects due to the thermal degradation process and to obtain curves that allow extracting pure kinetic information [22]. This procedure was applied to all the constant heating rate DSC results reported in the following. Fig. 2(b) reports the results obtained at heating rates ranging from 2.5 to 20 K min<sup>-1</sup>. As evident from the figure, all the curves show the presence of two exothermic peaks. Also the results of adiabatic calorimetry (see Fig. 3) show the presence of two exothermic peaks. No evidence of further decomposition phenomena was detected at higher temperatures by any of the three calorimetric techniques applied. Thus, the analysis of the results obtained by the three different calorimetric techniques applied support the presence of two exothermic decomposition stages in the Fenitrothion thermal degradation process. An average value of the heat of reaction associated with the two thermal decomposition peaks was calculated from DSC runs and is reported in Table 2.

Table 3 reports the results obtained from the analysis of ARC runs. The comparison of data in Tables 1 and 2 evidences that the three experimental techniques yield quite similar results, confirming the validity of the approach.

**Table 3**

Experimental conditions and main results obtained in the ARC experiment reported in Fig. 3.

Parameter	Value
Sample initial weight [g]	1.36
Sample final weight [g]	0.79
$\Phi$ – factor	2.8
Onset temperature of first decomposition step, $T_{0,1}$ [K]	409.3
Experimental adiabatic temperature rise, $\Delta T^{(1)}$ [K]	51.9
Equivalent actual adiabatic temperature rise, $\Phi \cdot \Delta T^{(1)}$ [K]	143.8
Pressure after first decomposition step, $P_{\text{max},1}$ [bar]	2.7
Heat generated in first decomposition step, $(-\Delta H_{R,1})$ [J g <sup>-1</sup> ]	303
Onset temperature of second decomposition step, $T_{0,2}$ [K]	471.7
Experimental adiabatic temperature rise, $\Delta T^{(2)}$ [K]	202.2
Equivalent actual adiabatic temperature rise, $\Phi \cdot \Delta T^{(2)}$ [K]	560.2
Pressure after second decomposition step, $P_{\text{max},2}$ [bar]	68.0
Heat generated in second decomposition step, $(-\Delta H_{R,2})$ [J g <sup>-1</sup> ]	1189

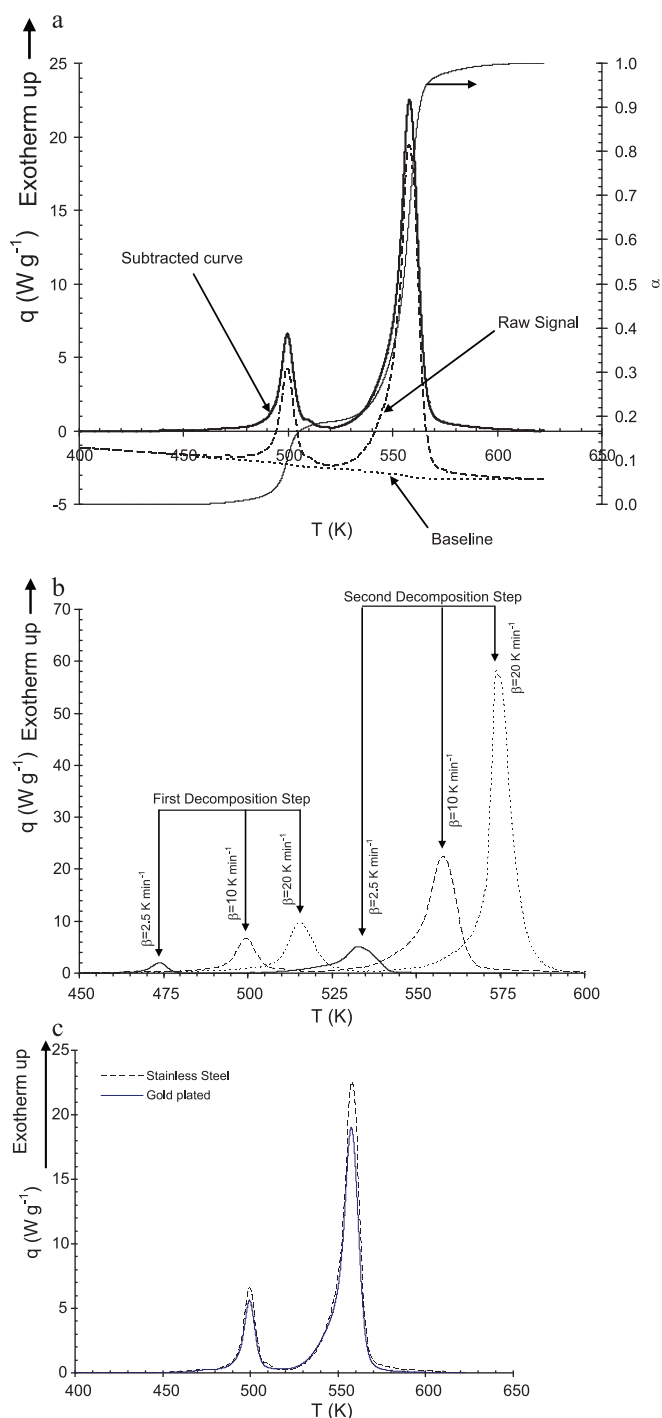
The possible influence of surface catalytic effects was also investigated. Fig. 2(c) reports the comparison of DSC runs carried out at 10 K min<sup>-1</sup> using respectively a stainless steel and gold-plated high pressure crucible. As evident from the figure, the two curves are very similar and no difference in the onset temperatures of the thermal decomposition processes is present. Moreover, the results of isothermal runs, discussed in the following, report a good correspondence of results obtained by DSC and by Radex, even if very different surface/volume ratios are present in these devices. Thus, it may be concluded that the presence of either metal surface or oxygen catalytic effects may be excluded.

The DSC data reported in Fig. 2(b) allowed us to obtain the Kissinger's plot for both degradation peaks, reported in Fig. 4. The following values were extrapolated for the apparent activation energy of the decomposition process: 89,657 J mol<sup>-1</sup> for the first stage of thermal degradation and 119,357 J mol<sup>-1</sup> for the second exothermic event.

#### 3.2. Decomposition products of Fenitrothion

The overall decomposition process of Fenitrothion leads to the evolution of incondensable gases and to the formation of a carbonaceous solid residue, as discussed in the following. However, at the end of the first degradation step, the situation is quite different: only few incondensable gases are present, while several partial decomposition products are formed in the condensed phase. This is evident from the data on maximum pressure reported in Tables 2 and 3.

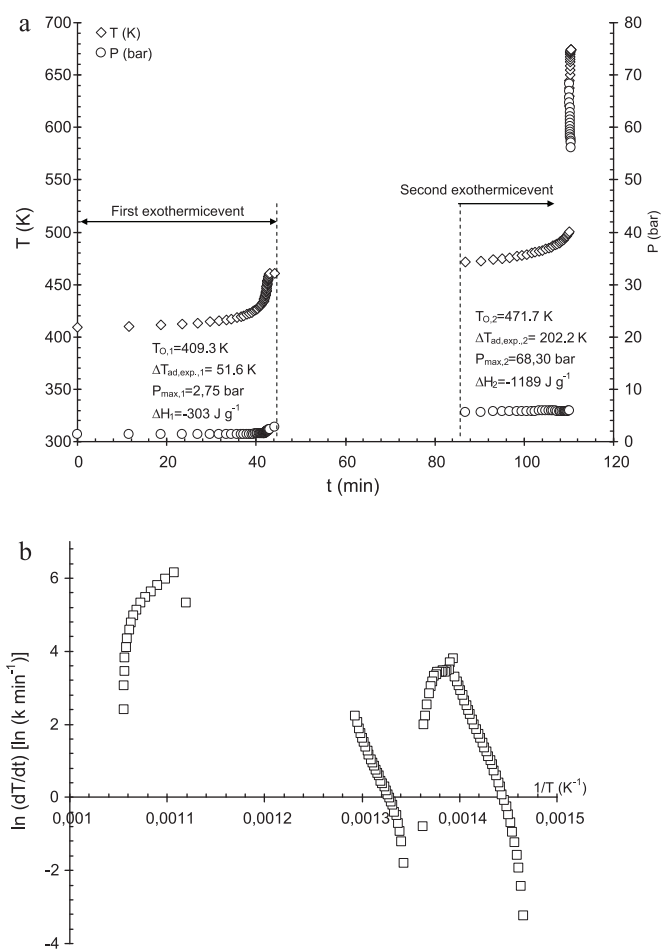
A GC/MS analysis was carried out on samples of about 2.0 g collected using 50 cm<sup>3</sup> of methanol at the end of two Radex runs performed in quasi-isothermal mode up to the complete conversion of the substrate. The samples were obtained heating the substrate both at 408 K for 3.5 h and at 423 K for 2.0 h. Table 1 reports the molecular structures of the intermediates identified. The GC/MS analysis also indicated the presence of a high molecular



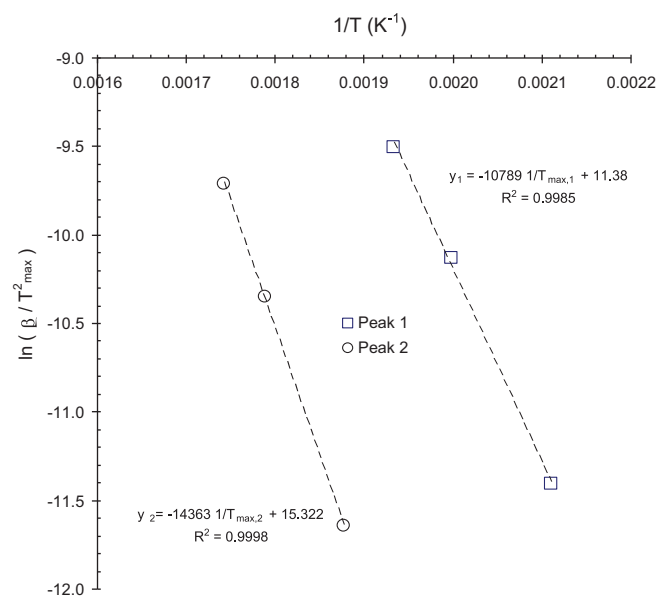
**Fig. 2.** (a) Raw DSC data (---), treated DSC data (—) and fictitious baseline (...) defined for the extrapolation of thermal effects related to thermal degradation process (left y-axis) obtained from a constant heating rate (10 K min<sup>-1</sup>) carried out on Fenitrothion. Sample conversion (—) calculated by Eq. (1) is also reported (right y-axis). (b) Treated DSC data obtained from DSC runs carried out on Fenitrothion samples at different heating rates. (c) Treated DSC data obtained from two constant heating rate runs (10 K min<sup>-1</sup>) carried out on samples of Fenitrothion (starting temperature: 323 K) using a stainless steel (solid curve) and a gold plated (dashed curve) high pressure crucibles.

weight compound for which it was not possible to identify a reliable structure. This is possibly an oligomer [16] that yields 4-methyl-nitrophenol as thermally or acidic decomposition.

The decomposition pathways of the first step of Fenitrothion thermal degradation were further investigated by isothermal DSC and further Radex runs. The heat flow data collected in isothermal

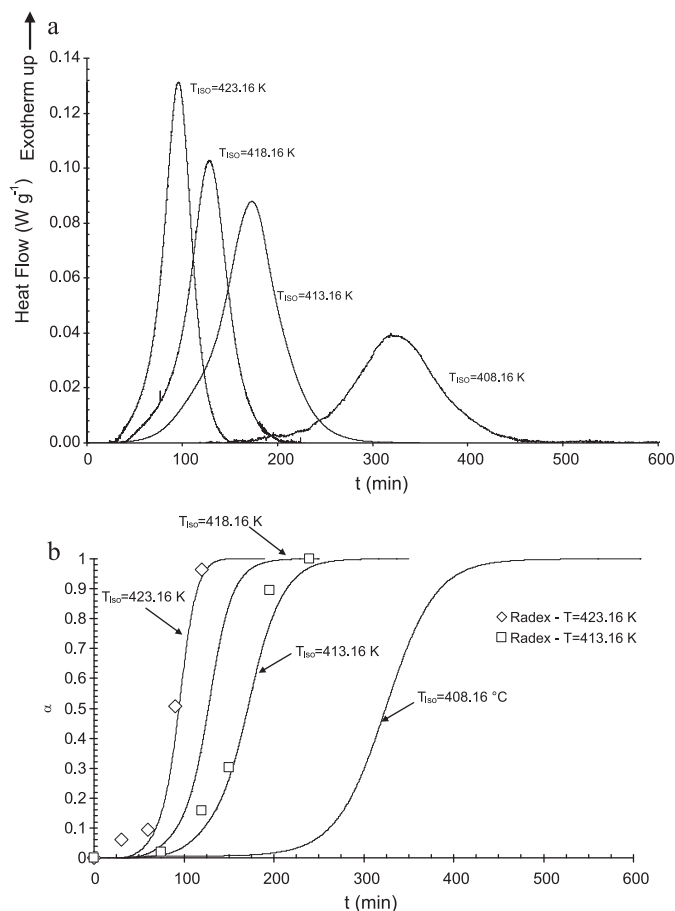


**Fig. 3.** (a) Results of an ARC adiabatic run performed on Fenitrothion: temperature–time and pressure–time profiles. (b) Self heating temperature rate plot ( $1/T$ ) during the ARC run on Fenitrothion reported in panel (a).



**Fig. 4.** Kissinger's plots obtained for the two stages of Fenitrothion thermal degradation from DSC data reported in Fig. 2(b).





**Fig. 5.** First step of Fenitrothion thermal degradation: (a) heat flow recorded in DSC experimental runs and (b) conversion versus time calculated from isothermal DSC runs (continuous lines) and isoperibolic Radex runs (symbols). Temperature of isothermal DSC and isoperibolic (quasi-isothermal) Radex runs are also reported on the plot.

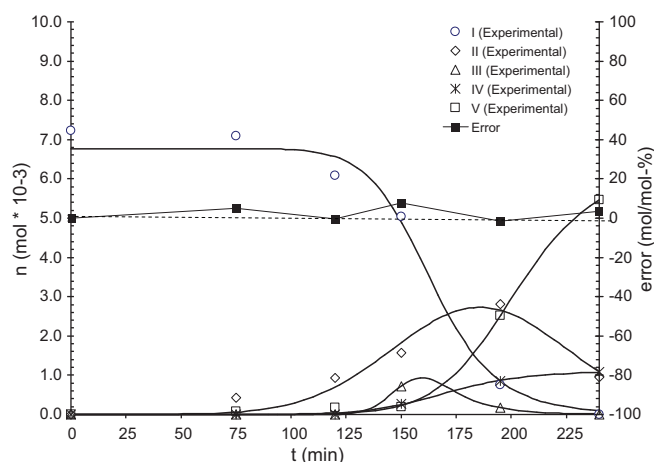
DSC runs are reported in Fig. 5(a). The apparent conversion of Fenitrothion was thus calculated assuming that the reaction heat is mostly generated in the decomposition of the substrate:

$$\xi = \frac{\int_0^t q(t) dt}{-\Delta H_R} \quad (1)$$

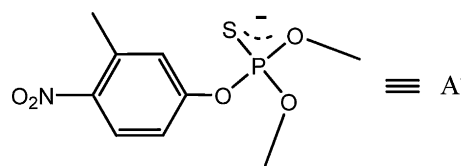
where  $q(t)$  is the heat flow recorded at time ( $t$ ) and  $(-\Delta H_R)$  is the heat of reaction calculated at the end of the DSC run. An average value of  $333 \pm 23\text{ J g}^{-1}$  was obtained, in sufficient agreement with data obtained from constant heating rate runs, reported in Table 2. Fig. 5(b) shows the results obtained applying Eq. (1) to the DSC curves reported in Fig. 5(a). The figure also reports the results of Radex isoperibolic runs carried out on Fenitrothion samples at 413 and 423 K.

Conversion data were obtained from HPLC chemical analysis on the residual sample. The results reported in Fig. 5(b) clearly show that a good agreement is present among DSC and Radex conversion data.

An insight on the formation of intermediates and final products is reported in Fig. 6. The figure shows Fenitrothion conversion and product yield data collected in isoperibolic (Radex) experiments carried out on samples of about 1.2 g of Fenitrothion at a temperature of 413 K using different reaction times. Sample conversion and product yields were determined by HPLC analysis of samples collected at the end of the run. Although practical limitations did not allow



**Fig. 6.** Fenitrothion conversion and decomposition product distribution obtained by HPLC analysis in a set of isoperibolic (Radex) runs carried out at  $T=413\text{ K}$  and different reaction times. Decomposition products (see Table 1):  $\circ$  [I],  $\diamond$  [II],  $\triangle$  [III],  $\ast$  [IV],  $\square$  [V] – oligomeric species,  $\blacksquare$  [error on material balance].



**Scheme 1.**

to assess the fate of phosphorus and sulfur, Fig. 6 shows that the experimental techniques used allowed the closure of mass balances with sufficient precision.

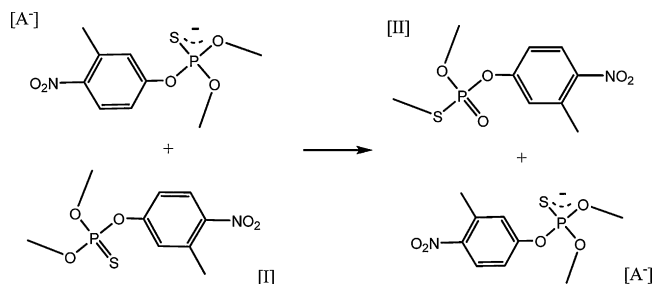
As shown in Fig. 6, S-ethyl isomer [II] is one of the first intermediates in the decomposition of Fenitrothion. This confirms previous results reported for the thermal behaviour of phosphorothionate compounds. There is a general agreement about the formation, of an intermediate anion during the isomerization process (Scheme 1) [23], which is successively S-alkylated reacting with a substrate molecule [24], as shown in Scheme 2.

The anion  $A^-$  can give also a nucleophilic attack at P centers with the release of other nucleophilic species ( $\text{CH}_3\text{S}^-$ ,  $\text{CH}_3\text{O}^-$ , 4-methyl-3-nitrophenate), as shown in Scheme 3.

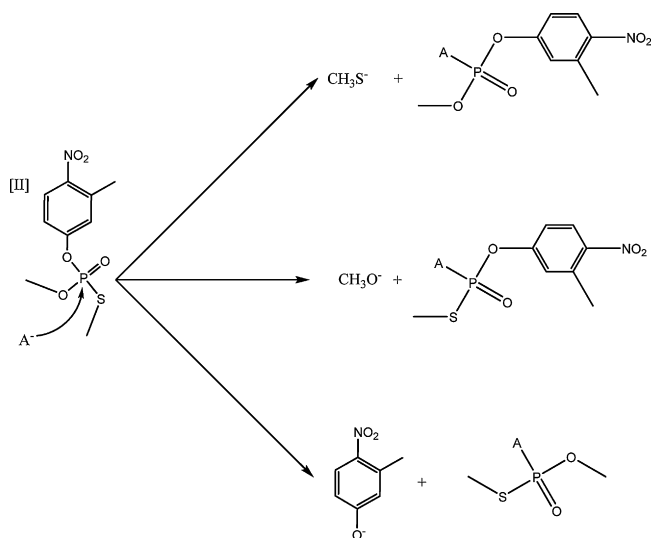
These species may attack all phosphorus-containing intermediates through a simple substitution (Scheme 4) or by a more complex, concerted process (Scheme 5).

The anions formed in the last reactions can eventually initiate an oligomerization process attacking the S-methyl isomer (Scheme 6).

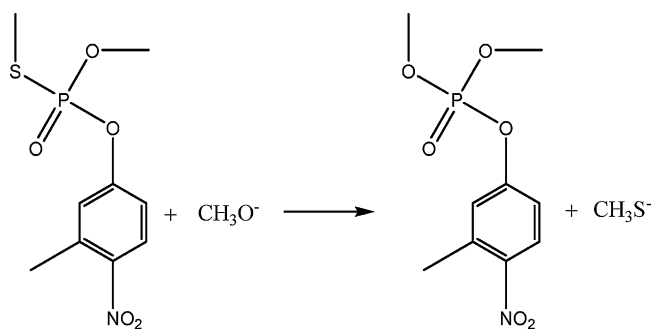
The presence in the reacting mixture of the “oligomeric” species can be explained as the result of the process reported in Scheme 6. It has to be stressed that the above thermal decomposition behaviour of Fenitrothion, resulting from experimental evidence, is quite



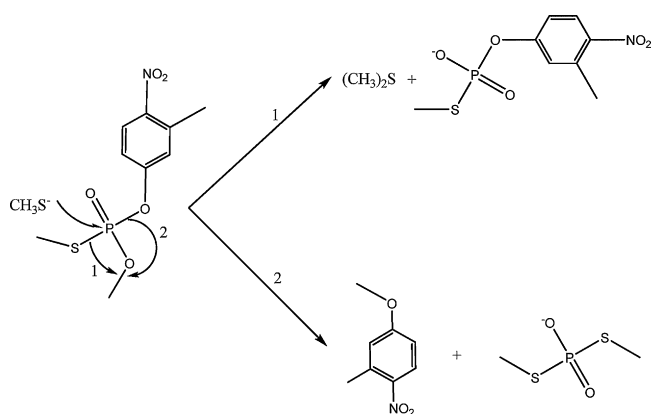
**Scheme 2.**



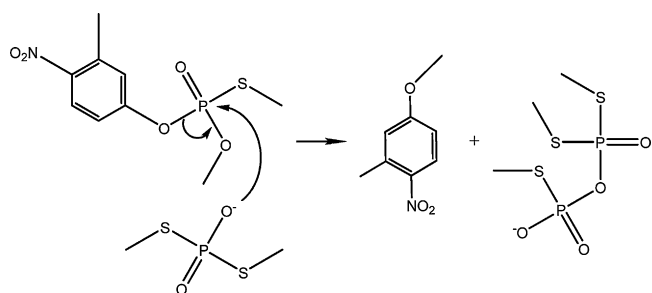
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

**Table 4**

Gas analysis on the sample collected from a complete ARC run performed on Fenitrothion.

Substance	Overall volume composition (v/v-%)	Composition excluding nitrogen Y (v/v-%)	Estimated % weight with respect to the initial sample
CO	30.20	37.25	8.64
CH <sub>4</sub>	24.55	30.28	4.01
CO <sub>2</sub>	15.63	19.28	7.03
C <sub>2</sub> H <sub>4</sub>	0.22	0.27	0.06
C <sub>2</sub> H <sub>6</sub>	0.38	0.47	0.12
Others <sup>a</sup>	10.09	12.45	4.54
N <sub>2</sub>	18.93	–	–
Total gases	100.00	100.00	24.4
Char			75.6

<sup>a</sup> As a working hypothesis, the molecular weight of propane was assumed for calculations to obtain the value in column 3.

similar to that reported for ethyl parathion [16], while it is strongly different from that reported for dimethoate [15].

With respect to the second decomposition stage, data in Figs. 2 and 3 show that a violent exothermic decomposition takes place, leading to the formation of gaseous products and of a solid residue. The solid residue (0.786 g of carbonaceous material: 75.6 (w/w-%) of the initial sample mass) recovered at the end of the dynamic Radex experiment of Fig. 2 was a char completely insoluble in acetone and methanol. No liquid or condensable thermal degradation product was identified besides the insoluble char, that could not be characterized by GC/MS analysis.

Table 4 reports the results of GC analysis of the gas phase sampled (280 cm<sup>3</sup> at ambient temperature, collected with a syringe) at the end of the ARC run of Fig. 3. Assuming that the only products of the decomposition are the insoluble char and the gases in Table 4, the table also reports the calculated weight % of each compound with respect to the original sample. Due to the low ecotoxicity profile of the product species formed at the end of the overall decomposition process, evident from Table 4, the attention was focused on the products of the first decomposition step, whose release represents the worst-case scenario.

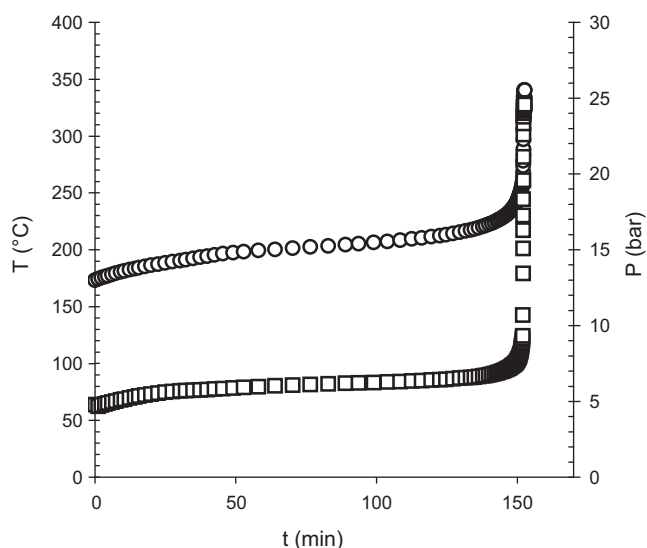
The explosive decomposition behaviour of methyl-nitrophenol is well known [25], while no indications are available for the thermal stability of the other decomposition products identified from the first decomposition step of Fenitrothion. A specific effort was dedicated to recover and characterize the thermal behaviour of the oligomeric species (V in Table 1) formed in the first decomposition step. An ARC run was carried out on 1.35 g of Fenitrothion (start temperature: 413 K, heat step temperature: 2.5 K, wait time: 10 min, thermal inertia,  $\Phi$ , equal to 2.80). In these conditions the onset temperature was recorded at 414 K, and the development of the first exothermic event involved an adiabatic temperature rise of 47.4 K. At the end of this phase the run was stopped and the condensable products were recovered using 50 cm<sup>3</sup> of methanol. Column chromatography allowed the recovery and purification of a sufficient quantity of “oligomeric” species (V in Table 1).

The results of an ARC run carried out on the oligomeric species separated by the above procedure (sample mass equal to 1.252 g; thermal inertia  $\Phi$  equal to 2.82) are reported in Fig. 7. As expected, the thermal decomposition of this compound is an exothermal event which leads to the formation of an incondensable mixture of gaseous compounds. It is important to note that the heat of decomposition of these “oligomeric” species accounts for 56% of the heat of decomposition measured during the second exothermic step of Fenitrothion thermal decomposition. Thus, the exothermic behaviour during the second decomposition step seems to be mainly due to the decomposition of nitro-organic “oligomeric” species as those shown in Table 1.



**Table 5**  
ECOSAR parameters considered in the eco-toxicological assessment (selected EC<sub>50</sub> values are reported in *italics*), and values of the decomposition product relative ecotoxicity index (DEI) calculated for products formed in the first decomposition step.

Compound	MW [g mol <sup>-1</sup> ]	EC <sub>50</sub> (green algae – 96 h) [mg (dm <sup>3</sup> ) <sup>-1</sup> ]	S [mg (dm <sup>3</sup> ) <sup>-1</sup> ]	Half time [h]	DEI baseline	DEI class-specific	
I	277.20	Esters, monothiophosphates Baseline toxicity	2.14 8.47	38.00	208	1.00	1.00
II	277.20	Esters Esters (phosphate) Baseline toxicity	25.20 146.10 41.52	94.20	208	4.90	68.27
III	261.20	Esters Esters (phosphate) Baseline toxicity	64.45 415.40 97.32	300.80	56	11.50	194.11
IV	153.40	Phenols Baseline toxicity	19.45 15.39	1190.00	208	1.82	9.09
V-(a)	508.40	Esters Esters (phosphate) Esters, dithiophosphates Baseline toxicity	2.11 8.81 3.08 4.55	0.07	208	0.54	1.44
V-(b)	755.60	Esters, monothiophosphates Esters, dithiophosphates Baseline toxicity	0.01 0.01 0.01	0.00	208	1.18 × 10 <sup>-3</sup>	4.67 × 10 <sup>-3</sup>
V-(c)	723.50	Esters Esters (phosphate) Esters, dithiophosphates Baseline toxicity	0.45 1.54 0.83 1.15	0.00	208	0.14	0.39
V-(d)	371.20	Esters Esters (phosphate) Esters, monothiophosphates Baseline toxicity	24.38 136.59 7.66 41.33	17.29	56	4.88	3.58



**Fig. 7.** Temperature and pressure profiles versus time during the ARC run performed on the “oligomeric” species formed in the first decomposition step of Fenitrothion. (○) Temperature; (□) pressure.

HPLC runs carried out on a sample recovered at the end of the adiabatic run reported in Fig. 7 and previously hydrolyzed at 423 K for 4 h by treatment with concentrated hydrochloric confirmed the presence of polymeric species having a molar ratio among phosphorus and 4-methyl-nitrophenate higher than 1.

### 3.3. Eco-toxicological assessment of decomposition products

The basic reason that motivated this study was to investigate the importance of antagonistic or synergistic effects on the overall eco-toxicity of the mixture of thermal degradation products with respect to what expected from the “sum” of single components.

The worst scenario (from a toxicological point of view), that is the formation and release of first step decomposition products was investigated. In order to understand the eco-toxicity of the single species formed in the first decomposition step, the EC<sub>50</sub> (green algae, 96 h) values for the single species were calculated using the ECOSAR freeware [26]. The results are reported in Table 5. A baseline EC<sub>50</sub> and values related to specific categories of compounds are provided by ECOSAR. Two values were selected for each compound: the baseline value of EC<sub>50</sub> and the score associated with the most appropriate class to which the compound of interest belongs. As shown in Table 5, a lower eco-toxicity profile generally results considering baseline EC<sub>50</sub> values.

Data in Table 5 allow the definition of a specific safety indicator to assess the environmental hazard of decomposition products. A Decomposition product Ecotoxicity relative Indicator (DEI) was defined for each of the decomposition products shown in Table 1 as the ratio of the EC<sub>50</sub> value calculated for the compound of interest with respect to that of the original substance.

The DEI values calculated for the intermediate decomposition products of Fenitrothion are reported in Table 5. Compounds II, III and IV in Table 1 show DEI values higher than 1. With respect to compound V, a DEI value lower corresponds to assumption (d), while the opposite situation occurs for structures (b) and (c). The DEI value of structure obtained by assumption (a) may be lower or higher than 1, depending on the value of EC<sub>50</sub> considered in the assessment (baseline or class-specific respectively). No conclusion can thus be drawn concerning the ecotoxicity of decomposition products unless the distribution of decomposition products distribution is completely known and quantitative data are available, that is not the case. It should also be remarked that the inclusion in the assessment of data concerning the gaseous compounds identified at the end of the decomposition (see Table 4) would not add significant pieces of information because a low eco-toxicological profile is associated to each of the compounds listed in Table 4.

In order to gather experimental data on the eco-toxicity of decomposition products, eco-toxicological bio-assays were carried

**Table 6**

Conditions used for the adiabatic runs devoted to collect the adiabatic samples used for ecotoxicological bioassay.

Sample	$m_{\text{Sample}}$ [g]	$m_{\text{Bomb}}$ [g]	$\Phi$	$T_0$ [K]	$T_{\text{Quenching}}$ [K]
A1	1.3610	12.0178	2.8	409.3	409.3
A2	1.6244	12.5531	2.5	411.0	416.1
A3	1.6225	12.5531	2.5	411.0	474.7

out applying the procedure described in Section 2 to samples collected at the end of both isothermal and adiabatic runs carried out on Fenitrothion at 413 K.

Several isothermal runs were carried out at 413 K by the procedure described in Section 2. Three adiabatic ARC runs were carried out holding the system in adiabatic conditions starting from the onset temperature of the first decomposition stage and quenching the sample at different temperatures (409, 416 and 475 K respectively). After forcing the instrument in the adiabatic mode at 409 K, adiabatic conditions were kept until the selected quenching temperature was obtained. The run was then stopped, the bomb cooled at ambient temperature and the sample recovered using 25 cm<sup>3</sup> of DMSO for the successive eco-toxicological assessment. Further details on these experimental runs are reported in Table 6.

The results of eco-toxicological assessments are reported in Table 7 for both the isothermal and the adiabatic samples. As shown in the table, a good agreement is present among the results of bio-assays carried out on the first-stage decomposition products obtained in isothermal and ARC runs. The experimental values of the EC<sub>50</sub>, as well as the calculated DEI, show an initial decrease followed by a relevant increase with time.

Table 8 shows a comparison with the theoretical values calculated combining the values obtained for single decomposition products (see Table 5) as follows:

$$EC_{50, \text{mix}} = \left( \frac{1}{n} \sum_{i=1}^m \frac{n_i}{EC_{50,i}} \right)^{-1} \quad (2)$$

where EC<sub>50,mix</sub> is the theoretical value calculated for the sample mixture,  $n$  is the initial number of moles of used in the experimental run,  $n_i$  is the number of moles of compound  $i$ th (see Fig. 6), and EC<sub>50,i</sub> is the calculated value of EC<sub>50</sub> for the  $i$ th compound (see Table 5). The results in Table 7 were obtained reporting both baseline and class-specific values and taking into account the four alternative structures considered for compound V. The data obtained give a hint on the possible structure of compound V. As a matter of fact, the non-decreasing trend of the EC<sub>50</sub> at times higher than 150 min or at temperatures higher than 416 K seems not coherent with structures V-(b) and V-(c), that should cause a decrease in the EC<sub>50</sub> after 120 min. On the contrary, a very good agreement is present among experimental and calculated data if structure V-(d) is considered.

**Table 7**

Experimental results of the bio-assays carried out on the residual sample collected during adiabatic and isothermal runs on Fenitrothion (I: isothermal runs; A: adiabatic runs).

Sample	Temperature [K]	Time (min)	EC <sub>50</sub> [mg (dm <sup>3</sup> ) <sup>-1</sup> ]	DEI
I0	298	0	1.90	1.00
I1	413	75	1.36	0.72
<b>I2</b>	<b>413</b>	<b>120</b>	<b>1.24</b>	<b>0.65</b>
I3	413	150	2.03	1.07
I4	413	195	1.93	1.02
I5	413	240	5.28	2.78
A1	409	0	2.00	1.05
<b>A2</b>	<b>416</b>	<b>33</b>	<b>0.70</b>	<b>0.37</b>
A3	475	59	9.50	5.00

Bold indicates the conditions (Adiabatic and Isothermal) corresponding to the lowest values found for the EC<sub>50</sub> and DEI.

**Table 8**  
Comparison between the experimental and calculated EC<sub>50</sub> values for samples collected during the first step of Fenitrothion decomposition. Calculated values were obtained using Eq. (2), conversion data in Fig. 6, baseline and the class-specific eco-toxicity profiles in Table 5, and assuming the four different possible structures of compound V postulated in Table 1.

Time (min)	EC <sub>50</sub> , experimental [mg (dm <sup>3</sup> ) <sup>-1</sup> ]	Overall EC <sub>50</sub> [mg (dm <sup>3</sup> ) <sup>-1</sup> ]		V-(a) (relative error)		V-(b) (relative error)		V-(c) (relative error)		V-(d) (relative error)	
		Baseline	Class-specific	Baseline	Class-specific	Baseline	Class-specific	Baseline	Class-specific	Baseline	Class-specific
0	1.90	8.47 (138%)	2.14 (-40%)	8.47 (138%)	2.14 (-40%)	8.47 (138%)	2.14 (-40%)	8.47 (138%)	2.14 (-40%)	8.47 (138%)	2.14 (-40%)
120	1.24	9.02 (289%)	2.49 (7%)	0.12 (-95%)	0.10 (-96%)	6.47 (179%)	2.19 (-6%)	6.47 (179%)	2.19 (-6%)	9.73 (319%)	2.52 (9%)
150	2.03	10.68 (180%)	3.12 (-18%)	0.12 (-97%)	0.10 (-97%)	7.24 (90%)	2.65 (-31%)	7.24 (90%)	2.65 (-31%)	11.72 (207%)	3.19 (-16%)
195	1.93	7.33 (102%)	4.66 (28%)	0.01 (-100%)	0.01 (-100%)	1.83 (-50%)	1.29 (-64%)	1.83 (-50%)	1.29 (-64%)	27.90 (669%)	9.03 (149%)
240	5.28	5.10 (-48%)	3.52 (-64%)	0.01 (-100%)	0.01 (-100%)	1.27 (-87%)	0.91 (-91%)	1.27 (-87%)	0.91 (-91%)	37.14 (275%)	8.93 (-10%)

Table 7 also reports the value of the DEI calculated from the experimental toxicological data. The DEI values show that in the early stages of thermal decomposition Fenitrothion leads to the generation of reacting mixtures more dangerous than the initial substrate. It is important to remark that the DEI values derived from isothermal samples are of the same order of magnitude of the DEI values determined for samples collected in adiabatic conditions. Therefore, the results obtained suggest that the more simple experimental procedure needed to produce isothermal samples may lead to results sufficiently consistent to define at least a valid indicator of the potential eco-toxicological hazard of decomposition products.

#### 4. Conclusions

The results of the present study show that in adiabatic conditions at temperatures higher than 409 K Fenitrothion undergoes a thermal decomposition process. The process is characterized by two exothermic events during which relevant amounts of gases are evolved. Intermediate and final thermal degradation products formed during isothermal and adiabatic thermal decomposition experiments were identified. The eco-toxicological profile of the decomposition products was assessed experimentally and compared to results obtained with a predictive software (ECOSAR). A specific index was defined to assess the change in ecotoxicity profile of decomposition products with respect to the original compound. The results evidence that in the early stages of decomposition Fenitrothion forms decomposition products that show a higher eco-toxicity than the original substrate. Moreover, the eco-toxicity of the mixture of decomposition products formed shows significant differences with respect to that expected as a “sum” of those of the single species present in the mixture. Thus, the results suggest the importance of experimental protocols allowing the assessment of the overall toxicity of mixtures of decomposition products formed in the loss of control of chemical industrial systems.

#### Acknowledgements

The authors would like to thank Mr. Andrea Bizzarro and Mr. Fernando Stanzione for their technical support and MIUR for the financial support in the frame of PRIN 2007 project.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.11.032.

#### References

- [1] L. Smith-Hansen, Risk analysis of a warehouse for the mixing repackaging and distribution of organic chemicals, *J. Loss Prev. Process Ind.* 1 (4) (1988) 233–236.
- [2] D.A. Kefalas, M.N. Christolis, Z. Nivolianitou, N.C. Markatos, Consequence analysis of an open fire incident in a pesticide storage plant, *J. Loss Prev. Process Ind.* 19 (1) (2006) 78–88.
- [3] G. Koller, U. Fischer, K. Hungerbühler, Assessing safety, health, and environmental impact early during process development, *Ind. Eng. Chem. Res.* 39 (4) (2000) 960–972.
- [4] V. Cozzani, S. Zanelli, Precursors of dangerous substances formed in the loss of control of chemical systems, *J. Hazard. Mater.* 65 (1999) 93–108.
- [5] V. Cozzani, M. Smeder, S. Zanelli, Formation of hazardous compounds by unwanted reactions in industrial accidents, *J. Hazard. Mater.* 63 (1998) 131–142.
- [6] M.H. Wood, The Seveso II experience in the application of generic substance criteria to identify major hazard sites, *J. Hazard. Mater.* 171 (2009) 16–28.
- [7] Council Directive 96/82/EC (“Seveso II”) concerning the control of major-accident hazards involving dangerous substances, *Off. J. Eur. Commun.*, L 10/13, Brussels, 14.1.97, <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:1996L0082:20031120:EN:PDF>.
- [8] R.J.A. Kersten, M.N. Boers, G. Opschoor, M. Cortes, Detection of hazardous reaction products during a thermal runaway, *Process Saf. Prog.* 22 (2) (2003) 99–104.
- [9] A. Lunghi, L. Gigante, P. Cardillo, V. Stefanoni, G. Pulga, R. Rota, Hazard assessment of substances produced from the accidental heating of chemical compounds, *J. Hazard. Mater.* 116 (1–2) (2004) 11–21.
- [10] K. Marsanich, F. Barontini, V. Cozzani, A. Creemers, R. Kersten, Different scale experimental techniques to approach the problem of substances generated in the loss of control of chemical systems: a study on ethyl diazoacetate decomposition, *J. Loss Prev. Process Ind.* 17 (2004) 9–22.
- [11] R. Andreozzi, I. Di Somma, A. Pollio, G. Pinto, R. Sanchirico, Toxicity of unwanted intermediates and products formed during accidental thermal decomposition of chemicals, *J. Hazard. Mater.* 150 (2008) 433–437.
- [12] F. Barontini, S. Zanelli, V. Cozzani, L. Gigante, A. Lunghi, R. Rota, P. Cardillo, Experimental strategies for the identification of substances formed in the loss of control of chemical industrial processes, *J. Loss Prev. Process Ind.* 21 (4) (2008) 407–422.
- [13] IPCS INCHEM, International Programme on Chemical Safety, <http://www.inchem.org/documents/ehc/ehc/ehc133.htm>.
- [14] M.R. Sovizi, K. Anbaz, Kinetic investigation on thermal decomposition of organophosphorous compounds—N,N-dimethyl-NO,N0-diphenylphosphorodihydrazidic and diphenyl amidophosphate, *J. Therm. Anal. Calorim.* 99 (2010) 593–598.
- [15] R. Andreozzi, G. Ialongo, R. Marotta, R. Sanchirico, The thermal decomposition of dimethoate, *J. Hazard. Mater.* 64 (1999) 283–294.
- [16] R. Andreozzi, G. Ialongo, R. Marotta, R. Sanchirico, Thermal decomposition of ethyl parathion, *J. Loss Prev. Process Ind.* 12 (1999) 315–319.
- [17] M. Luginbuehl, I. Priestley, A comparison of DSC and Radex for the investigation of safety parameters for inhomogeneous systems, in: *Proc. Hazards XIX Process Safety and Environmental Protection*, Manchester, England, 27–30 March, 2006, 2006, pp. 572–585.
- [18] EPA, Guidance for preparing standard procedures (SOPs), EPA/240/B-01/004, 2001.
- [19] H.W. Nichols, Growth media-freshwater, in: J.R. Stein (Ed.), *Handbook of Phycological Methods*, Cambridge University Press, Cambridge, 1973, pp. 7–24.
- [20] EPA, Ecological effects test guidelines OPPTS 850.5400 Algal toxicity, Tiers I and II, 1996.
- [21] T.J. Norberg-King, A Linear Interpolation Method for Sublethal Toxicity: the Inhibition Concentration (IC) Approach Version 2.0., U.S. Environmental Protection Agency, Duluth, MN, 1993.
- [22] B. Roduit, C. Borgeat, B. Berger, P. Folly, B. Alonso, J.N. Aebischer, F. Stoessel, Advanced kinetic tools for the evaluation of decomposition reactions—determination of thermal stability of energetic materials, *J. Therm. Anal. Calorim.* 80 (2005) 229–236.
- [23] T. Maeda, M. Kawashima, Y. Ogasawara, K. Tsuji, Thermal decomposition of OO-dimethyl O-(3-methyl-4-nitrophenyl) phosphorothioate – autocatalytic decomposition mechanism – decomposition of organophosphorus pesticides (Part 2), *J. Pest. Sci.* 7 (3) (1982) 341–347.
- [24] M. Eto, L.C. Tan, Y. Oshimar, K. Takehara, The isomerization of alkyl phosphorothionates induced by carboxylic acid amides, *Agric. Biol. Chem.* 32 (1968) 656–663.
- [25] L. Bretherick, *Handbook of Reactive Chemical Hazards*, Butterworths, London, 1990.
- [26] ECOSAR, Program Risk Assessment Division (7403), U.S. Environmental Protection Agency, <http://www.epa.gov/oppt/newchems/tools/21ecosar.htm>.